

Enhancement of the Na_xCoO_2 thermopower due to electronic correlations

P. Wissgott¹, A. Toschi¹, H. Usui², K. Kuroki² and K. Held¹

¹ *Institute for Solid State Physics, Vienna University of Technology, 1040 Vienna, Austria*

² *University of Electro-Communications 1-5-1 Chofugaoka, Chofu-shi Tokyo 182-8585, Japan*
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Using the merger of local density approximation and dynamical mean field theory, we show how electronic correlations increase the thermopower of $\text{Na}_{0.7}\text{CoO}_2$ by 200%. The newly revealed mechanism is an asymmetric shift of (quasi) electrons and holes away from the Fermi level, concurrent with an asymmetry of the respective (group) velocities. Exploiting this effect in bandstructure and correlation engineering may lead to a substantial increase of the thermoelectric figure of merit.

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Climate change and the prospective oil peak necessitate the discovery of new green energy sources. One possibility in this context is to convert hitherto unused excess heat into electrical energy using thermoelectrics [1]. For a real breakthrough and a widespread application of this technology however, thermoelectric figures of merit $ZT \gtrsim 3$ are needed [2, 3]. Recently, some advance was brought about through phonon [4] and bandstructure engineering [5] so that $ZT \gtrsim 1$ could be achieved. Pushing ZT much higher requires however a thermoelectric leap, which is most likely brought about by discovering a new class of materials – at least in the case of (high-T) superconductivity scientific progress went along this line with the discovery of novel correlated materials. At commercially available $ZT \lesssim 1$, thermoelectrics are already applied in niche markets such as radioisotope power systems for satellites [6] where reliability is more important than efficiency; and the car industry is taking encouraging first steps to use thermoelectrical generators [7]. The materials presently used in industry are mainly Te-based and have been investigated most thoroughly [8] with respect to optimizing their thermoelectric properties, including the aforementioned phonon [4] and bandstructure engineering [5].

The good thermoelectric properties of Te-based materials are related to their physics of slightly doped semiconductors with a low effective mass and high mobility of the charge carriers [2, 8]. A possible improvement are compounds with a pudding-mold type of bandstructure as those of Na_xCoO_2 [9] and LiRh_2O_4 [10] – two oxides with remarkably good thermoelectric properties [11–14].

Another route to good thermoelectric properties is through electronic correlations [15, 16] which can renormalize bands most substantially, so that narrow quasi-particle bands with a high density of states emerge. The renormalization factor is most dramatic in heavy Fermion systems which have particularly narrow Kondo resonances, modeled e.g. by a periodic Anderson model [17]. While one might expect the narrowest resonances to be most suitable for thermoelectrics, there is a trade-off since increasing the temperature T above the Kondo temperature (essentially the resonance width) will eventually

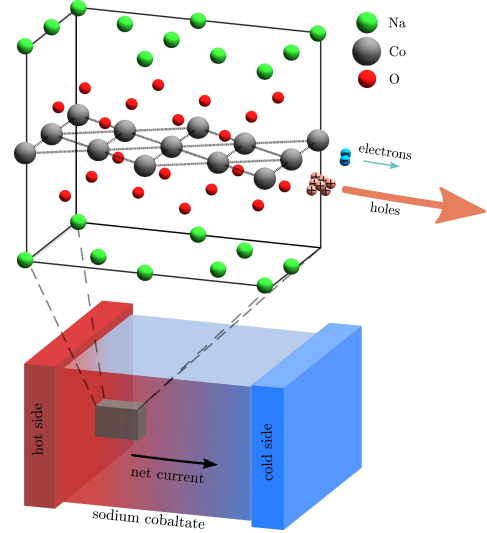


FIG. 1: (Color online) Scheme of a Na_xCoO_2 thermoelectric module and its crystal structure. The charge carriers are confined to the hexagonal layers of Co atoms, which are inequivalent because of the (disorderly distributed) Na ions above and below.

If we apply a heat gradient, electrons and holes alike are diffusing from the hot to the cold side resulting typically in a very small net current. For a good thermoelectric, we need however a large net current, i.e. a huge asymmetry between electron and hole diffusion.

Due to the pudding-mold bandstructure in Na_xCoO_2 , the group velocity of the holes is already considerably larger than that of the electrons, as indicated by the larger orange (dark gray) arrow. Electronic correlations additionally shift electrons away from the Fermi level, as visualized by the fewer blue electrons and the narrower width of the blue (light gray) arrow. As both effects add up, the electron is much smaller than the hole current leading to the net current displayed and hence, to the good thermoelectric properties of Na_xCoO_2 .

smear out the resonance itself.

In this paper, we demonstrate by means of Na_xCoO_2 , which already has a favorable pudding-mold bandstructure, that the complementary effect of electronic correlations can dramatically increase the thermopower, see Fig. 1. Needed are inequivalent orbitals or sites, so that electronic correlations can change the “particle-hole balance” of the system drastically, shifting more electrons

away from the Fermi level than holes.

For treating electronic correlations and bandstructure effects on an equal level, we employ the local density approximation+dynamical mean field theory (LDA+DMFT) approach [18–20] and calculate thermoelectric response functions as described in [21]. Previous LDA+DMFT calculations for Na_xCoO_2 [22–24] focused on the spectral function, whereas we naturally aim at the transport properties of this material. Starting point is a tight-binding fit to the LDA bandstructure [25] for the $\text{Co } a_{1g}$ band within the hexagonal CoO_2 layers, see Fig. 1. Considering transport properties (e.g. the thermopower S), the other d -bands can be neglected at a first approximation. In fact, LDA predicts already that these bands are almost filled, and this result is also confirmed experimentally, since e_g hole pockets are absent in angular resolved photoemission spectroscopy (ARPES) [26, 27]. There are $x < 1$ Na^+ ions per formula unit, which we consider to be randomly distributed with a Na atom or vacancy in trigonal prismatic coordination to the Co sites. As it has been suggested in Ref. 23, this gives rise to a disorder potential on the Co sites – since the positively charged Na^+ attracts the Co-electrons. This disorder potential is of essential importance for the strong electronic correlations of the Co d -electrons; and as in Ref. 23, we take an disorder potential of $\Delta\varepsilon = 0.55$ eV. Our resistivity calculation (inset of Fig. 4) *a posteriori* confirms that a disorder potential of this strength is present; otherwise the experimental value of the resistivity at room temperature, mainly due to the disorder (and not to the electron-electron scattering) could not be explained [28]. Our model Hamiltonian hence reads

$$H = - \sum_{(ij),\sigma} t_{ij} c_{j\sigma}^\dagger c_{i\sigma} + U \sum_i c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow} + \Delta\varepsilon \sum_{i \in \text{vac},\sigma} c_{i\sigma}^\dagger c_{i\sigma},$$

where $c_{i\sigma}^\dagger, c_{i\sigma}$ are creation and annihilation operators of the a_{1g} electrons, with i the site index and σ the spin index and t_{ij} denotes the hopping parameter from site i to site j , obtained from a tight-binding fit to LDA data [25, 29]. For the Coulomb repulsion within the a_{1g} orbitals we take a value $U = 3.5$ eV and for the Na disorder potential $\Delta\varepsilon = 0.55$ eV as in [23]. As a DMFT impurity solver we use quantum Monte Carlo simulations, where the Na-disorder is included at the level of the coherent potential approximation CPA. For the calculation of the response functions we proceed as in [21], using a Taylor-fit to extract the low energy behavior of the self energy on the real axis.

Fig. 2 shows our k -resolved and k -integrated spectral function. For example along path $\bar{\text{H}}\bar{\text{A}}\bar{\text{F}}\bar{\text{K}}$ through the Brillouin zone, the LDA bandstructure $\varepsilon(k)$ (gray line in 2(a)) vaguely resembles the form of a pudding mold. The advantage of the pudding-mold bandstructure is the highly asymmetric group velocity of the electrons and holes above and below the Fermi level, respectively. This velocity is given by the slope $v_g(k) = \partial\varepsilon(k)/\partial k$ which,

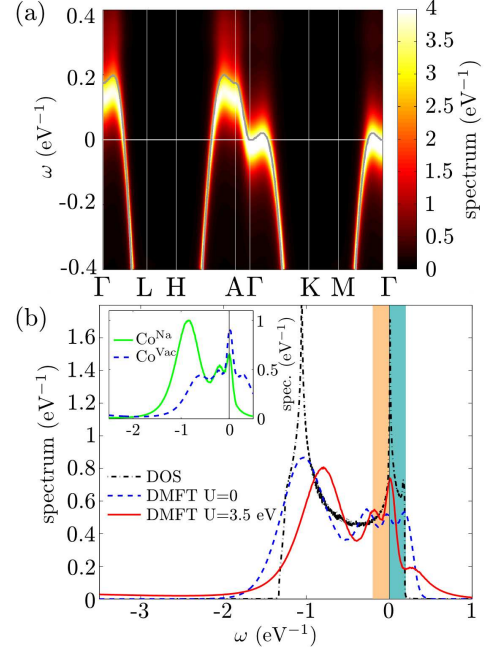


FIG. 2: (Color online) (a) LDA+DMFT k -resolved spectrum of $\text{Na}_{0.7}\text{CoO}_2$ at 290 K around the chemical potential ($\omega \equiv 0$), along with the tight-binding band extracted from the LDA calculation (light gray). (b) LDA+DMFT k -integrated spectra for $T = 290$ K and $x=0.7$ with and without interaction U and disorder potential $\Delta\varepsilon$ (dotted line: $U=0$, $\Delta\varepsilon=0$; dashed line: $U=0$, $\Delta\varepsilon=0.55$ eV; solid line: $U=3.5$ eV, $\Delta\varepsilon=0.55$ eV). For fixed $U=0$, an increasing disorder potential $\Delta\varepsilon=0 \rightarrow 0.55$ eV leads to more symmetric but lower spectral weight in the highlighted interval $\pm 8k_B T$ around the Fermi level. For fixed $\Delta\varepsilon=0.55$ eV, increasing $U=0 \rightarrow 3.5$ eV recovers spectral weight on the hole side $\omega < 0$ whereas electrons $\omega > 0$ lose spectral weight in the relevant (highlighted) area. The inset shows the k -integrated spectra at the two inequivalent lattice sites, with and without an adjacent Na^+ ($T=290$ K, $U=3.5$ eV, and $\Delta\varepsilon=0.55$ eV).

because of the pudding mold, dramatically changes at the Fermi level at least in the $\bar{\text{F}}\bar{\text{K}}$ direction (not so much along $\bar{\text{H}}\bar{\text{A}}$). The LDA density of states, on the other hand, is higher above the Fermi level (for electrons) than below (for holes), see (Fig. 2(b)). Hence, the asymmetry in v_g which increases the thermopower S is partially compensated by the asymmetry in the density of states. In Fig. 1 there would be, on the LDA level, more electrons than holes contributing.

The thermoelectric figure of merit is defined as $ZT = S^2/(\rho\kappa)T$, with the temperature T , the electrical resistivity ρ and the thermal conductivity $\kappa = \kappa_{el} + \kappa_{ph}$ where κ_{el} , κ_{ph} denote the electronic and phononic contributions, respectively. By use of Kubos formulas in DMFT [30], one finds $\rho = 1/K_0$, $S = -\frac{k_B}{T} \frac{K_1}{K_0}$ and $\kappa_{el} = (K_2 - K_1^2/K_0)/T$ with the correlation functions

$$K_n = (-1)^{n+1} \frac{2\pi e^{2-n}}{V} \sum_k v_g^2(k) \int d\omega A^2(k, \omega) \frac{\partial f}{\partial \omega} \omega^n, \quad (1)$$

where V is the unit cell volume, $f(\omega)$ is the Fermi-Dirac distribution function. Comparing Eq. (1) for $n = 0$ and $n = 1$, it becomes clear that due to the factor ω in K_1 , electron ($\omega > 0$) and hole contributions ($\omega < 0$) push S in opposite directions. A high electron-hole asymmetry is hence mandatory for getting a large $|S|$.

Before turning to the electronic correlations, let us first discuss the effect of disorder (dashed line of Fig. 2(b)), not yet switching on the interaction U . As one can see, the spectral weight around the Fermi energy is smeared out because of the disorder and the spectral weight is most dramatically reduced. As one might expect from Eq. (1), this is very unfavorable for the thermopower. Actually, it is reduced from the disorder-free value [9] to only $S=25 \mu\text{V/K}$ without interaction U . In Fig. 1, we visualize this by a narrower arrow for both electron and hole contribution and a smaller net current.

This radically changes if electronic correlations are taken into account. Their effect can be best understood by hands of the inset of Fig. 2(b), which shows the k -integrated Co spectrum locally resolved for sites with and without an adjacent Na^+ ion. The Coulomb interaction drive the vacancy-adjacent Co sites more towards half-filling. Consequently, electronic correlations become stronger which reflects in the sharp quasiparticle resonance and Hubbard-like side bands. In contrast, the Na^+ -adjacent Co sites become almost completely filled and are only weakly correlated. Together, the shift of the Na^+ -adjacent Co spectrum below the Fermi energy and the strong renormalization of the vacancy-adjacent Co sites yields a higher spectral weight on the hole than on the electron side. This asymmetry now *adds* to the $v_g(k)$ asymmetry, in stark contrast to the original LDA spectral weight. Note, that the velocities itself are, to first order, not renormalized by the electronic correlations since these are a property of the underlying LDA orbitals. A complete overview of the effect of disorder and correlation on the transport properties is given in Tab. I.

To further illustrate the changes induced by correlation, we introduce a thermopower spectral density $s(k, \omega) = -\frac{k_B}{TK_0} \frac{2\pi e}{V} v_g^2(k) A^2(k, \omega) \frac{\partial f(\omega)}{\partial \omega} \omega$, which integrated over k and ω yields the thermopower S (Fig. 3). The contour lines show that, upon (artificially) switching on the proper U , thermopower spectral weight is taken away from the electron side. As one can see in Fig. 2(b) it is transferred further away from the Fermi level. In contrast, the reduction of spectral weight on the hole side is much smaller and close to the Γ point $s(k, \omega)$ is even enhanced. This correlation-induced electron-hole imbalance strongly enhances the thermopower (S increases by 200% w.r.t. the case of $U=0$).

Finally, we present in Fig. 4 the calculated thermopower S as a function of T for various doping; the corresponding resistivity is shown in the inset. Our LDA+DMFT results agree well with experiment for both quantities including the doping and T dependence. The

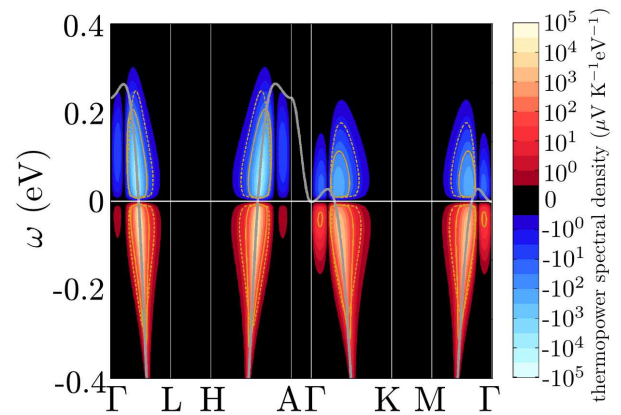


FIG. 3: (Color online) Thermopower spectral density $s(k, \omega)$ for $T=290 \text{ K}$, $U=3.5 \text{ eV}$ and $\Delta\varepsilon=0.55 \text{ eV}$ together with the tight-binding band extracted from the LDA data (gray). Positive values $s > 0$ (red for $\omega < 0$) contributed by holes dominate negative values $s < 0$ (blue for $\omega > 0$) contributed by electrons. The electronic contribution is more sensitive to correlation which is emphasized by the values $s = \pm 10^2 \mu\text{V K}^{-1} \text{ eV}^{-1}$ highlighted by an isocurve, comparing $U=3.5 \text{ eV}$ (solid) and $U=0$ (dashed).

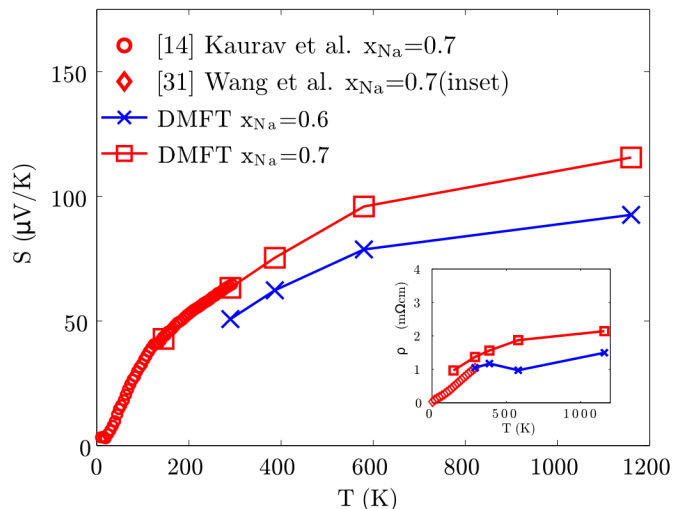


FIG. 4: (Color online) Thermopower S as a function of temperature for different doping $x_{\text{Na}} = 0.6, 0.7$ showing good agreement to the experiment of Kaurav *et al.* [13]. The inset shows the corresponding result for the resistivity compared to experiments by Wang *et al.* [31].

large thermopower of Na_xCoO_2 originates from the pudding mold band structure and is further enhanced by electronic correlations. The physical mechanism for the large resistivity on the other hand, is the disorder scattering.

From our calculations we conclude that Na_xCoO_2 is far from optimal for thermoelectric properties. On the bandstructure side, there is still no strong electron-hole asymmetry for the group velocities in the ΓL and HA di-

parameters	$\rho(\text{m}\Omega\text{cm})$	$S(\mu\text{V}/\text{K})$	$\kappa_e(\text{mW}/\text{cm K})$	$S^2/\rho(\mu\text{W}/\text{K}^2 \text{ cm})$	$Z (10^{-3} \text{ K})$	ZT
$U = 0, \Delta\varepsilon = 0$	0.21	54	36.8	13.8	0.135	0.039
$U = 3.5 \text{ eV}, \Delta\varepsilon = 0$	0.31	66	27.4	13.7	0.146	0.042
$U = 0, \Delta\varepsilon = 0.55 \text{ eV}$	2.51	25	2.9	0.2	0.004	0.001
$U = 3.5 \text{ eV}, \Delta\varepsilon = 0.55 \text{ eV}$	1.37	63	6.5	2.9	0.040	0.012
experiment	1.04[31]	64[13]	4.0[32]	3.9[13, 31]	0.053[13, 31, 32]	0.015[13, 31, 32]

TABLE I: Thermoelectric and transport properties for single crystalline $\text{Na}_{0.7}\text{CoO}_2$ at 290 K. For the computed figure of merit $Z = S^2/\rho(\kappa_{ph} + \kappa_e)$, we take the experimental phononic thermal conductivity $\kappa_{ph} = 66\text{mW}/\text{cm K}$ [32]. The electronic part of the thermal conductivity κ_e is calculated with the correlation functions from Eq. (1) and estimated experimentally by the Wiedemann-Franz law. Note that there are no free parameters and that only disorder ($\Delta\varepsilon$) and correlation (U) together describe all experimental values reasonably well.

rection due to the three dimensionality, see Fig. 2. Hence, the electron contribution (blue in Fig. 2(b)) still reduces the thermopower considerably. This can be improved by bandstructure engineering the pudding mold form, e.g., by expanding the c-axis length via intercalation. Second, disorder broadens the LDA substantially and dramatically decreases the Seebeck coefficient as well as the conductivity $\sim 1/\rho$. There is hence a high potential for further increasing S , e.g., by realizing a similar physical situation on the basis of inequivalent orbitals or superstructures without disorder. Last, but not least, we have shown the crucial role correlation can play, not only because of the narrowing of the coherent excitations but also in strengthening the particle-hole imbalance. Given the high sensitivity of correlated systems to small changes of the external conditions and recent advances in engineering man-made heterostructures of correlated materials, there is plenty of room for improving this correlation effect further.

We can thus conclude from our study of transport properties in Na_xCoO_2 that, if properly combined, bandstructure and correlation effects (as those present in transition metal d and rare earth f orbitals) can considerably improve the thermoelectric properties of materials. Jointly, engineering bandstructure and correlations hence opens a new route to further enhance S (and possibly ZT) up to the levels required for a widespread technological applications.

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